

**Table S1 Band gap, energy and Ce-O bond changes of CeO<sub>2</sub>(111) with and without U corrections**

U-value (eV)	0	2.0	4.5	5.0
Band gap (eV)	1.56	1.59	1.42	1.47
Band gap change (eV)	0	+0.03	-0.12	-0.09
Energy (eV)	-25573.36	-25559.63	-25544.27	-25541.47
Energy change (eV)	0	+13.73	+29.09	+31.89
Ce-O bond (Å)	2.34	2.34	2.35	2.35
Ce-O bond change (Å)	0	0	+0.01	+0.01

**Table S2 Bond lengths (Å) of undoped and Cu-doped CeO<sub>2</sub>(111) after the formation of oxygen vacancies**

	CeO <sub>2</sub> (111) with a V <sub>OS</sub>	CeO <sub>2</sub> (111) with a V <sub>OSS</sub>	Cu/CeO <sub>2</sub> (111) with a V <sub>OS</sub>	Cu/CeO <sub>2</sub> (111) with a V <sub>OSS</sub>
Ce3(Cu)-O1	2.26	2.25	2.03	1.99
Cu-O2	2.26	2.25	2.03	1.99
O1-Ce1	2.26	2.25	2.21	2.15
O2-Ce2	2.26	2.25	2.21	2.15
O3-Ce1	2.26	2.25	2.26	2.28
O3-Ce2	2.26	2.25	2.26	2.28

**Table S3 Bond lengths (Å) of O<sub>2</sub> adsorbed on the V<sub>OS</sub>**

	Before optimization	After optimization
O <sub>f1</sub> -O <sub>f2</sub>	1.22	1.30
O <sub>f2</sub> -Cu	2.99	1.90
Cu-O1	2.03	3.16
Cu-O2	2.03	3.17
O <sub>f1</sub> -Ce1	1.52	2.78
O <sub>f1</sub> -Ce2	2.75	2.78
O <sub>f2</sub> -Ce1	2.62	3.70
O <sub>f2</sub> -Ce2	2.74	3.80
O <sub>f1</sub> -V <sub>OS</sub>	0	0.44

**Table S4 Bond lengths (Å) of O<sub>2</sub> adsorbed on the V<sub>OSS</sub>**

	Before optimization	After optimization
O <sub>f1</sub> -O <sub>f2</sub>	1.22	1.47
O <sub>f2</sub> -O1	1.71	1.44
O <sub>f1</sub> -Cu	2.13	2.36
O <sub>f2</sub> -Cu	2.13	3.10
Cu-O1	1.99	3.54
Cu-O2	1.99	3.66
O <sub>f1</sub> -V <sub>OSS</sub>	0.02	0.76

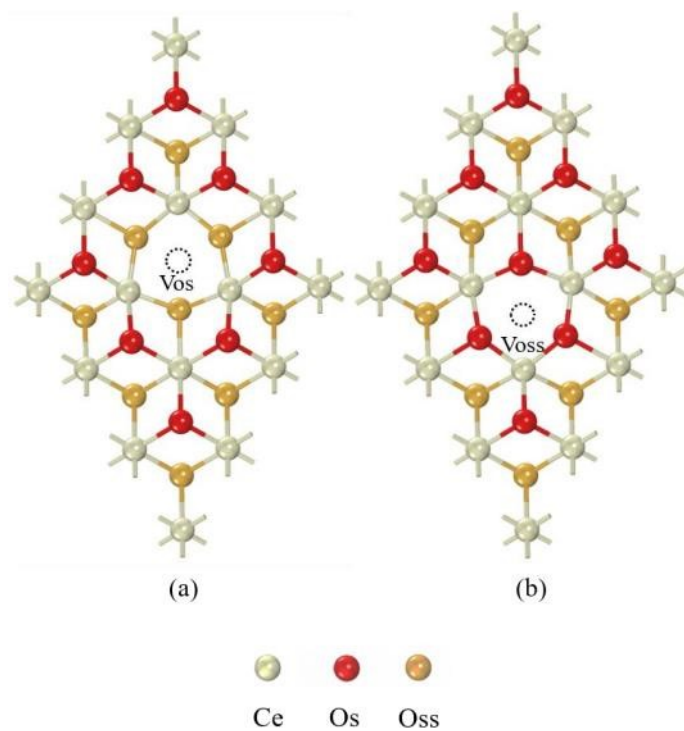


Figure S1 Top view: (a) CeO<sub>2</sub>(111) with a V<sub>OS</sub>; (b) CeO<sub>2</sub>(111) with a V<sub>OSS</sub>

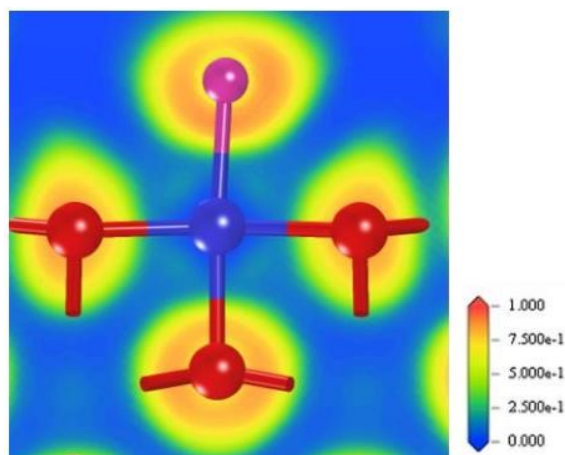
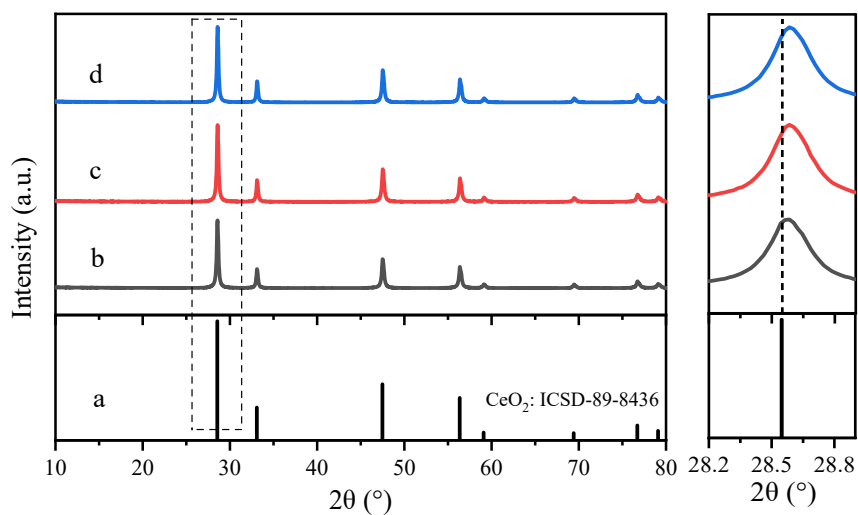


Figure S2 Electron localization diagram for the adsorption of O<sub>2</sub> on the V<sub>OS</sub> for Cu/CeO<sub>2</sub>(111)



**Figure S3 XRD patterns of CeO<sub>2</sub> and CuO/CeO<sub>2</sub> catalysts calcined at different temperatures: (a) CeO<sub>2</sub>; (b) CuCe400; (c) CuCe500; (d) CuCe600 (CuO/CeO<sub>2</sub> catalysts calcined at 400 °C, 500 °C and 600 °C were named as CuCe400, CuCe500 and CuCe600, respectively.)**